CHEM 331
Physical Chemistry
Revision 1.0

Chemical Equilibrium

Chemical Reaction

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

A, B, C, D are Chemical Species
a, b, c, d are Stoichiometric Coefficients

Or

$$0 = -\,a\,A - b\,B + c\,C + d\,D$$

Or, Formally

$$0 = \sum_i \nu_i J_i$$

J_i are Chemical Species
ν_i are Stoichiometric Coefficients

Description of Reaction Progress

$$n_i = n_i^o + \nu_i \xi$$

n_i is the number of moles of J_i
n_i^o is the initial number of moles of J_i
ξ is the Reaction Advancement

At Equilibirum

$$n_{i,e} = n_i^o + \nu_i \xi_e$$

Condition of Equilibrium

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G = \sum_i \nu_i \mu_i$$

At Equilibrium

$$\Delta G = 0$$

Equilibrium Constants

$\Delta G^o = - RT \ln(K)$

$K = \prod {a_i}^{\nu_i}$

<u>Ideal Gases</u>

$K_P = \prod \left(\frac{P_i}{P^o}\right)^{\nu_i} = \prod {P_i}^{\nu_i}$ P^o is 1 *bar* or 1 *atm*, depending on the Table

$= K_x P^{\Delta\nu}$ *P* must be in the same units as P^o

$= K_c (RT)^{\Delta\nu}$ *c* must be in units of mol/L

<u>Real Gases</u>

$K = \prod \left(\frac{f'}{P^o}\right)^{\nu_i} = K\gamma\, K_P$

$= \prod {\gamma_i}^{\nu_i} \prod {P_i}^{\nu_i}$

<u>Condensed Phase Solutions</u>

$K = \prod {a_i}^{\nu_i} = K\gamma\, K_x$

$= \prod {\gamma_i}^{\nu_i} \prod {x_i}^{\nu_i}$ $a_i = \gamma_i x_i$; μ^* reference state

$= K\gamma\, K_x$

$= \prod {\gamma_i}^{\nu_i} \prod {x_i}^{\nu_i}$ $a_i = \gamma_i x_i$; μ^{**} reference state

$= K\gamma\, K_m$

$= \prod {\gamma_i}^{\nu_i} \prod \left(\frac{m_i}{m^o}\right)^{\nu_i}$ $a_i = \gamma_i m_i/m^o$; μ^{***} reference state

$= K\gamma\, K_c$

$= \prod {\gamma_i}^{\nu_i} \prod \left(\frac{c_i}{c^o}\right)^{\nu_i}$ $a_i = \gamma_i c_i/c^o$; $\mu^{\square}$ reference state

Temperature Dependence of K

$$\ln K(T) = \ln K(T_o) - \int_{T_o}^{T} \frac{\Delta H^o}{R}\, d\left(\frac{1}{T}\right)$$

$$= \ln K(T_o) - \frac{\Delta H^o}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

Assumes ΔH^o is constant

Le Chatelier's Principle

$$0 = -\frac{\Delta H}{T}\, dT_e + \Delta V\, dP_e + G_e''\, d\xi_e$$

$$G_e'' = \left(\frac{\partial^2 G}{\partial \xi^2}\right) > 0$$

Constant P

$$\left(\frac{\partial \xi_e}{\partial T}\right)_P = \frac{\Delta H}{T\, G_e''}$$

Constant T

$$\left(\frac{\partial \xi_e}{\partial P}\right)_T = -\frac{\Delta V}{G_e''}$$